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Technical Report
to the
Office of Naval Research

Project NR 051-258

POTENTIAL AT ZERO CHARGE FOR REVERSIBLE
AND
IDEAL POLARIZED ELECTRODES

by

Paul Ruetschi and Paul Delahay

Report No. 19

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PAUL RÜETSCHI AND PAUL DELAHAY

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ABSTRACT

The potential at zero charge for an ideal polarized electrode, as measured with respect to some reference electrode, varies linearly with the work function of the metal, while this potential for a reversible electrode is independent of the nature of the electrode. This observation is verified experimentally for Ag, Cd, Cu, Ga, Hg, Ni, Pb, Pt, and Tl in the case of ideal polarized electrodes and for Ag, Au, Bi, Cu, Hg, and Pt for reversible electrodes. It is shown that the difference between the Volta potentials from electrode to solution for an ideal polarized electrode at zero charge is approximately -0.33 volt, and that the difference between the Galvani potentials is equal to the surface potential of the electrode. The difference of Volta potentials for a reversible electrode at zero charge varies linearly with the electronic work function of the metal.

INTRODUCTION

The potential at which the charge at the interface electrode - solution is equal to zero can be determined experimentally for conditions under which electron transfer across the interface is either possible or virtually impossible. Determinations in which electron transfer is possible are carried out with a reversible electrode. Measurements for which electron transfer is virtually impossible are made with what Grahame[2,3] has called an "ideal polarized electrode". A mercury electrode in an electrolyte to which no mercurous ions

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[1] Postdoctoral fellow 1953-54.

[2] D.C. Grahame and R.B. Whitney, J. Am. Chem. Soc., 64, 1548 (1942).

[3] D.C. Grahame, Chem. Revs., 41, 441 (1947).

or other reducible or oxidizable substance are added behaves almost as an ideal polarized electrode[3]. Potentials at zero charge, as measured against some reference electrode, may be very different (as much as one volt) according to whether one or the other method is applied. The reason for this difference was the object of a controversy between Billiter[4] and Palmaer[5], but the argument was never settled. The fundamental difference between the two types of measurement is discussed quantitatively in this paper.

The relationship between potential at zero charge and work function of the metal has already been discussed by several authors. Veselovsky[6] pointed out that the difference between the zero charge potentials for silver and mercury electrodes is virtually equal to the difference between the work functions of these metals. According to Grahame[3], Frumkin[7] expressed similar ideas more than twenty years ago. Vasenin[8] recently pointed out that a plot of potential at zero charge (measured with respect to some reference electrode), against work function for various metals has a slope smaller than unity. This result was accounted for by the action of multipoles of the solvent at the interface electrode-solution. As far as we know no distinction between data obtained with ideal polarized and reversible electrodes is made by these Russian authors.

In the following discussion we shall use the Galvani, Volta, and surface

4 J. Billiter, Z. Elektrochem., 8, 638 (1902); Z. physik. Chem., 51, 166 (1905).

5 W. Palmaer, Z. Elektrochem., 9, 754 (1903); Z. physik. Chem., 59, 129 (1907).

6 V.J. Veselovsky, Acta Physicochim. U.R.S.S., 11, 815 (1939).

7 A.N. Frumkin, Colloid Symposium Annual, 7, 89 (1930).

8 R.M. Vasenin, Zhur. Fiz. Khim., 27, 878 (1953).

potentials introduced by Lange[9-11]. The definition of these potentials will be briefly recalled. The Galvani or inner potential, φ, of a phase is defined as the electrical work involved in bringing a unit positive charge from infinity into the phase. The Volta or outer potential, ψ, of a phase is defined as the work required to bring a unit positive charge from infinity to a point just outside the phase where the influence of the image forces is negligible, i.e. at about 10^{-4} cm. from the surface of the phase in a state equivalent to the Schottky state[12]. The meaning of the expression "just outside the phase" is discussed by Adam[13]. The surface potential, χ, of a phase is defined by the electrical work involved in transferring a unit positive charge from a point just outside the phase into the phase. The difference between the Volta potentials of two phases is a well-defined and measurable quantity, while the corresponding difference of Galvani potentials cannot be measured and, according to Guggenheim[14], cannot even be defined. Strehlow[15], although he recognizes that differences of Galvani potentials cannot be measured, adopts the less extreme and more fruitful approach that such differences of potential

9 E. Lange, Handbuch der Experimentalphysik, Vol.12, Pt.2, Akademische Verlagsgesellschaft, Leipzig, 1933, 267 ff.

10 O. Klein and E. Lange, Z. Elektrochem., 43, 570 (1937).

11 E. Lange, ibid., 55, 76 (1951); 56, 94 (1952).

12 W. Schottky and Rothe, Handbuch der Experimentalphysik, Vol.12, Pt 2, Akademische Verlagsgesellschaft, Leipzig, 1928, 145 ff.

13 N.K. Adam, The Physics and Chemistry of Surfaces, 3rd Ed., Oxford University Press, London, 1941, p.303.

14 E.A. Guggenheim, J. Phys. Chem., 33, 842 (1929); 34, 1758 (1930).

15 H. Strehlow, Z. Elektrochem., 56, 119 (1952).

could in principle be calculated.

The above potentials are related by the equation[9-11]

$$\varphi = \psi + \chi .$$ (1)

The e.m.f. across a complete electrochemical cell can be computed from Galvani or Volta potentials as indicated in Fig.1, where V represents either φ or ψ .

IDEAL POLARIZED ELECTRODES

Consider the cell of Fig.1 and assume that metal I – solution II is an ideal polarized electrode. The phases III and IV form a normal calomel electrode, which is connected to metal I. The e.m.f. of the cell is the sum of the differences of the Galvani or Volta potentials. The e.m.f. is positive when the electrode I on the left is positive with respect to the electrode I on the right. The difference of potential for the interface I-II depends on the adsorption of ions and on the orientation of multipoles of the solvent (water) in II. The charge at the interface can be changed by applying a voltage to the cell, and the e.m.f. corresponding to zero charge at the interface I-II can be determined by several methods described in Butler's review[16]. For example, the e.m.f. of the cell of Fig.1, when metal I is mercury, is in the immediate vicinity of -0.50 volt in the absence of an electrocapillary active species in solution[3].

If metal I is changed, it is observed that the e.m.f. of the cell corresponding to zero charge varies. A plot of experimental values of the e.m.f.

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[16] J.A.V. Butler in <u>Electrical Phenomena at Interfaces</u>, J.A.V. Butler Ed., Methuen, London, 1951, pp 30-74.

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of the cell against the work function[17] of metal I is shown in Fig.1.[18]
A few experimental potentials at zero charge are not plotted in Fig.2 because
of the uncertainty on the corresponding work functions. Thus, data[19] for
zinc (-0.63 volt) and tellurium (+0.61 volt) are not shown. Data for plati-
num are uncertain, and the potential at zero charge, + 0.28 volt, instead of
the value +0.42 volt plotted in Fig.2, is quoted by Butler[20]. The value of
the work function of platinum is, at any rate, rather uncertain[17]. The points
(solid circles) of Fig.1 cluster along a line having a slope of one. If one
accepts this value of the slope, the difference of Volta potentials for an
ideal polarized electrode is constant. The argument is as follows.

The difference of Volta potentials $\psi_{IV} - \psi_I$ in the expression of the
e.m.f. of the cell of Fig.1 varies as the metal is changed. In view of the

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footnote

[17] Work function values from Handbook of Chemistry and Physics, C.D. Hodgman
Ed., Chemical Rubber Publishing Co., Cleveland Ohio, 1951, pp 2128-2131.

[18] Potentials at zero charge: T. Veslovsky, Acta Physicochim., U.R.S.S.,
11, 815, (1939) for Ag; J. Billiter, Z. Elektrochem., 14, 624 (1908) for
Cu; E. Murtazaev and J. Gorodetzkaja, Acta Physicochem., U.R.S.S., 4, 75
(1936) for Ga; D.C. Grahame, Chem. Revs., 41, 441 (1947) for Hg; R. Par-
sons, Z. Elektrochem., 55, 113 (1951) for Ni; T.J. Borisova, B.V. Ershler,
and A. Frumkin, J. Phys. Chem., U.S.S.R., 22, 925 (1948) for Pb; J. Bil-
liter, Z. Elektrochem., 8, 638 (1902) for Pt; A. Frumkin, J. Colloid Sci.,
1, 277 (1946), and T. Borisova, B.V. Ershler, and A. Frumkin, Zhur. Fiz.
Khim., 22, 925 (1948) for Tl; A. Frumkin, Vestnik Moskov Univ., 7, No 9,
37 (1952) for Cd.

[19] See last reference in footnote 18.

[20] See ref.16, p.41.

definition of the work function, one has[11, 21]

$$\psi_{IV} - \psi_I = -\left(W_{IV}' - W_I \right) \qquad (2)$$

where the W's are the work functions expressed in volts. The difference between the work functions accounts for the experimental variations of the e.m.f. at zero charge for different metals, and consequently the term $\psi_I - \psi_{II}$ in the expression of V (Fig.1) is independent of the nature of metal I. In other words the difference of Volta potentials at zero charge for ideal polarized electrodes is constant regardless of the nature of the electrode. It should be noted that this conclusion was reached from experimental results, and was not deduced from a priori considerations. The difference of Volta potentials at zero charge can be evaluated as follows.

The difference of Volta potentials for the normal calomel electrode $\psi_{Hg} - \psi_{III}$, as measured by Klein and Lange[10], is +0.17 volt. Since the e.m.f. for the cell of Fig.1 is practically -0.50 when the metal I is mercury, the difference of Volta potentials, $(\psi_I - \psi_{II})_{z.c.}$, for the ideal polarized electrode at zero charge is -0.33 volt. This value is approximate since the datum of Klein and Lange is affected by the errors resulting from experimental difficulties.

The calculation of the difference of Galvani potentials would require the value of the difference between the surface potentials of phases I and II. The surface potential for aqueous solutions against an inert gas was evaluated as -0.36 volt by Strehlov[15]. It is essentially independent of the electrolyte[15, 22] (no electrocapillary active substance present) at least for not too concentrated solutions, say, less than 0.1 M. The surface potential

21   P. Van Rysselberghe, J. Chem. Phys., 21, 1550 (1953).

22   A. Frumkin, J. Chem. Phys., 7, 552 (1939).

primarily results from the orientation of water multipoles – mainly dipoles – with their positive poles toward the inert gas. On the basis of the value $\chi_{II} = -0.36$ volt one deduces from (1) the difference between Galvani potentials

$$\varphi_I - \varphi_{II} = \left(\psi_I - \psi_{II}\right) + \left(\chi_I - \chi_{II}\right) \qquad (3)$$

or, in view of the value −0.33 volt for the difference between the ψ's (see above) at zero charge,

$$\left(\varphi_I - \varphi_{II}\right)_{Z.C.} = -0.33 + 0.36 + \chi_I \qquad (4)$$

This shows that the difference between Galvani potentials for an ideal polarized electrode at zero charge is virtually equal to the surface potential of the metal. Again, it should be emphasized that there is some uncertainty on the data used in this calculation.

The same conclusion can be deduced from the value of the difference of Galvani potentials of 0.495 volt calculated by Latimer, Pitzer, and Slansky[23] for the normal calomel electrode. As was pointed out by several authors[15, 21, 22, 24, 25], the surface potential of mercury must be added to the calculated value of 0.495 volt. Thus

$$\left(\varphi_{Hg} - \varphi_{III}\right)_{N.C.E} = +0.50 + \chi_{Hg} \qquad (5)$$

23 W.M. Latimer, K.S. Pitzer, and C.M. Slansky, J. Chem. Phys., 7, 108 (1939).

24 W.C. Burgers, Chem. Weekblad, 39, No 16-17, 1 (1942).

25 R. Piontelli, Int. Committee Electrochem. Therm. Kin., Proc. 2nd Meeting, Tamburini, Milan, 1951, pp.344-369.

If metal I of Fig.1 is mercury, the e.m.f. of the cell, which is the sum of the Galvani potentials, is -0.50 volt[3]. Thus

$$- 0.50 = \left(\varphi_I - \varphi_{II} \right)_{z.c.} + \left(\varphi_{III} - \varphi_{Hg} \right)_{N.C.E.} \qquad (6)$$

if one makes the justifiable assumption that the difference of Galvani potentials between the solutions II and III can be neglected in this approximate calculation[11]. By combining (5) and (6) one obtains

$$\left(\varphi_I - \varphi_{II} \right)_{z.c.} = \chi_{Hg} , \qquad (7)$$

which is precisely equation (4) as written for the particular case of mercury.

REVERSIBLE ELECTRODES

Potentials at zero charge for reversible electrodes have been measured by varying the ratio of the activities of the species involved in the reversible electrode until zero charge is obtained. Experimental results[26] are given in Fig.2, which shows conclusively that the potential at zero charge is independent of the work function of the metal. This result can be explained by considering the cell of Fig.1. If metal I is changed the difference between the Volta potentials for phases IV and I varies because of variation of the work function of metal I. However, the difference between the Volta potentials

---

[26] Experimental data: K. Bennewitz and J. Schulz, Z. physik. Chem., 124, 115 (1926) for Ag and Cu; K. Bennewitz and A. Delijannis, ibid., 154, 113 (1931) for Hg; W.A. Patrick and C.L. Littler, J. Phys. Chem., 54, 1016 (1950) for Ag, Au, and Pt; H.S. Oel and H. Strehlow, Z. physik. Chem. (Frankfurt, N.F.), 1, 241 (1954) for Bi. The latter authors also confirmed the previous results for Hg, Au, Pt, and Cu.

between I and II is changed by the same amount as for IV and I, because electrons are now transferred across the interface I-II. This is the situation encountered in the measurement of reduction potentials with an inert electrode. The e.m.f. of the cell is then independent of the nature of the inert electrode. One deduces from the foregoing considerations that the difference of Volta potentials for reversible electrodes at zero charge varies linearly with the electronic work function of the metal.

CONCLUSION

Differences between experimental potentials at zero charge as obtained with reversible and ideal polarized electrodes can be accounted for on the basis of considerations based on Galvani, Volta, and surface potentials.

ACKNOWLEDGMENT

LIST OF FIGURES

METAL	SOLUTION	$Hg_2^{''}$ in KCl	MERCURY	METAL
I	II	III	IV	I

$$E = (V_I - V_{II}) + (V_{II} - V_{III}) + (V_{III} - V_{IV}) + (V_{IV} - V_I)$$

FIG. 1

ELECTRONIC WORK FUNCTION (VOLTS)

POTENTIAL AT ZERO CHARGE (VOLTS VS. N.H.E.)

○ REVERSIBLE ELECTRODE

● POLARIZED ELECTRODE

FIG. 2

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